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PROSPECTS OF USING ZEOLITE ROCKS OF SIBERIA IN SILICATE MATERIALS

V. N. Smirenskaya[1] and V. I. Vereshchagin[1]

The results of integrated studies of zeolite rocks from the Sakhaptinskoe and Kholinskoe deposits are shown and the prospects of using clinoptilolite-bearing zeolite materials in mixed gypsum-zeolite, zeolite-magnesium, and lime-zeolite binders are determined.

According to contemporary data, natural zeolites belong to the typical mineral rocks of Siberia and the Far East and are mainly made up of minerals of the heulandite – clinoptilolite series. A. S. Kossovskaya proposed to name this group of zeolite minerals the "clinoptilolite-heulandite group" [1], since clinoptilolite is the most common rock-forming mineral after silica, feldspar, and clays and is present virtually in all zeolite rocks that can be used in industrial production [2].

A typical feature of zeolite deposits is that their degree of zeolitization fluctuates within a wide range. According to the existing classification, these rocks are called zeolitized when the content of zeolite mineral is 10 – 15%, zeolite-bearing when the content is from 15 to 50%, and zeolite when the content is 50% or more. The possible areas of application of the first two types of rocks depend not only on the properties of zeolite but those of associate minerals as well. Deposits with content of zeolite minerals over 50% are promising for industrial use. The traditional application areas of natural zeolites are related to their ion-exchange and adsorption properties and mostly relate to two fields: industrial ecology and agriculture.

Natural zeolites are currently being explored with the aim of a fuller practical application of these rocks in various technologies, which contributes to industrial working of the deposits. The most topical research is oriented to using natural zeolites as local siliceous materials for such resource-consuming sectors as housing construction, and this concerns all silicate technologies: ceramic, glass, and binding materials [3 – 7].

The present study summarizes the results of the long-time research carried out at the Silicate Technology Department of Tomsk Polytechnic University in developing zeolite-containing binders of increased water resistance based

on zeolite rocks of the Kholinskoe (Chita Region) and Sakhaptinskoe (Krasnoyarsk Region) deposits representing different genetic types.

Two genetic types of rocks prevail in Siberia and the Far East: volcanohenic-sedimentary diagenetic type and hydrothermal-metasomatic type of volcanic origin. Zeolite rocks of the Sakhaptinskoe deposit belong to the first type and are mostly formed over ash tuff and tuffite of dacite composition, and rocks of the Kholinskoe deposit belong to the second type and are formed over acid tuff of liparite-dacite composition. However, the initial tuff underwent substantial mineral transformations with time, whereas the chemical composition of the parental rocks changed insignificantly. The informative chemical characteristics accepted in practice in the study of natural zeolites include not only the average chemical composition of rocks but also the calculated values of the molar oxide ratios, which are criteria for evaluation of the chemical composition of zeolite rocks (Tables 1 and 2).

The weight content of oxides in the rocks converted into formulas expressing the molar ratios of oxides yielded the following: $0.5Na_2O \cdot K_2O \cdot 2.5CaO \cdot 4.5Al_2O_3 \cdot 32.5SiO_2 \cdot 17H_2O$ for the Sakhaptinskoe zeolite and $1.5Na_2O \cdot 1.5K_2O \cdot CaO \cdot 4Al_2O_3 \cdot 32SiO_2 \cdot 18H_2O$ for the Kholinskoe zeolite. A comparison of the chemical analysis data of zeolite rocks with the ideal formulas of zeolite minerals, i.e., heulandite $0.25(Na_2O, K_2O) \cdot 4CaO \cdot 4.5Al_2O_3 \cdot 27SiO_2 \cdot 24H_2O$ and clinoptilolite $Na_2O \cdot K_2O \cdot CaO \cdot 3Al_2O_3 \cdot 30SiO_2 \cdot 20H_2O$, suggests that heulandite is predominant in Sakhaptinskoe deposit rocks and clinoptilolite prevails in Kholinskoe rocks.

The zeolite mineralization of Sakhaptinskoe and Kholinskoe rocks is represented by heulandite and clinoptilolite, which belong to the same structural group. According to the data in [2, 8], the main physicochemical properties of these minerals are similar, and it is evident that as the aluminum content in the skeleton of the zeolite mineral grows, its ex-

[1] Tomsk Polytechnic University, Tomsk, Russia.

TABLE 1

Rock	Weight content, %								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	Δm_{calc}
Sakhaptinskoe:									
brown	66.01	12.51	2.36	0.34	2.27	1.66	1.04	3.24	10.28
green	64.84	12.77	2.46	0.35	2.50	1.79	0.63	3.20	11.12
Kholinskoe	67.70	11.97	1.04	0.08	1.37	0.42	2.52	3.63	11.39

change capacity increases and at the same time its chemical and thermal resistance decrease. The physicochemical properties of clinoptilolite $(Na, K)_4CaAl_6Si_{30}O_{72} \cdot 20H_2O$ and heulandite $(Na, K)Ca_4Al_9Si_{27}O_{72} \cdot 24H_2O$ are indicated in Table 3.

The isostructural similarity of the minerals determines the proximity of their diffraction characteristics [2, 9, 10]; therefore, clear identification of these minerals by the x-ray method is difficult. More significant distinctions between heulandite and clinoptilolite are manifested in their thermal properties. The DTA curve of the Sakhaptinskoe zeolite sample has an additional endothermic effect with a maxima at 270°C in the range of the main endothermic effect, which correlates with the phase transition of heulandite-A into heulandite B and is the main identifying attribute of a substantial quantity of heulandite in a rock.

Intense and constant processes of dehydration of zeolite reversibly proceed within a temperature range of 20 – 700°C and have a deep smooth endothermic effect typical of clinoptilolite with maxima at 100°C (Kholinskoe rock) and 130°C (Sakhaptinskoe rock). The increased intensity of the endothermic effect and the higher temperature of adsorbed water removal point to a more extended and defective mineral structure of the Sakhaptinskoe zeolite rock. The slight endothermic effect at 400 – 450°C is related to dehydration of montmorillonite and that at 560 – 580°C to the phase transformation of β-quartz into α-quartz. The exothermic effect at 480 – 520°C is due to the crystallization of the amorphous component of the zeolite rock.

To determine the specific mineralogical composition of the considered rocks using the method of rational chemical analysis, individual minerals were fully or partly extracted from the rock and treated with respective reactants (distilled water, hydrochloric acid, alkali or soda ash solutions, phosphoric acid, etc.). It was established that Sakhaptinskoe zeolite contains 12.3% free silica and Kholinskoe zeolite has 8.4%, and the content of free quartz is 8.6 and 6.1% and that of soluble alumina is 3.64 and 4.15%, respectively. This points to the potential chemical activity of the rocks.

Using a set of methods including petrography, x-ray phase, differential-thermal, and chemical analysis, the relative content of minerals in the zeolite rocks was identified. The minerals in the Sakhaptinskoe mineral rock are arranged in the following sequence with respect to their quantities; clinoptilolite → heulandite → quartz → montmorillonite →

TABLE 2

Parameter	Sakhaptinskoe rock		Kholinskoe rock
	brown	green	
Total molar content, %:			
SiO_2 and Al_2O_3	78.52	77.67	79.67
R_2O and CaO	6.55	6.33	7.52
R_2O and RO	8.21	8.12	7.94
Total molar content of R_2O, %	4.28	3.83	6.15
Molar ratio, %:			
Si : Al	4.40	4.32	4.81
$SiO_2 : Al_2O_3$	8.94	8.65	9.64
$Na_2O : Al_2O_3$	0.14	0.09	0.35
$K_2O : Al_2O_3$	0.29	0.27	0.33

TABLE 3

Parameter[*]	Clinoptilolite	Heulandite
Ratio Si : Al	4.2 – 5.5	2.70 – 3.75
True density, g/cm³	1.71	1.69
Ion exchange capacity (calculated/actual), mg · equ/g	2.7/2.0	3.1/2.8
Volume of free intracrystalline space, cm³/cm³	0.28 – 0.35	0.30 – 0.39
Chemical resistance in 1 N HCl, %	80 – 90	60 – 70
Heat resistance, °C	650 – 700	450 – 500

[*] Monoclinic syngony.

feldspar; in the Kholinskoe rock the sequence is: clinoptilolite → cristobalite → montmorillonite → quartz → heulandite → feldspar.

The specifics of zeolitic rocks are also manifested under heating. In particular, about 50% water is removed in heating the Sakhaptinskoe zeolite sample to 200°C, 80% is lost up to 400°C, and nearly 90% of the total water content at 500°C. The Kholinskoe zeolite is dehydrated by 60% in heating to 300°C and becomes virtually totally dehydrated by 700°C.

Based on the results of the integrated thermal analysis of zeolites, the following thermal treatment intervals were selected for activation of zeolite: 80 – 100, 160 – 200 and 650 – 700°C. The intensity of the diffraction reflections of clinoptilolite with $d = 0.892$ nm on the x-ray patterns of the zeolite heat-treatment products decreases to one-eighth when heated to 700°C, and the integral width for this reflection increases 2 and 4 times, respectively, when heat-treated in the

TABLE 4

Parameter	Rock	
	Sakhaptinskoe	Kholinskoe
True density, kg/m^3	2200	2360
Bulk density (fraction $0 - 5$ mm), kg/m^3:		
in loose state	760	900
in consolidated state	1830	2000
Zeolite layer porosity (fraction $0 - 5$ mm), %:		
in loose state	65.5	62.0
in consolidated state	16.8	15.3
Mohs hardness	$3.0 - 3.5$	$3.5 - 4.5$
Crushing strength, MPa	22.6	28.9
Abradability, %	18	14
Natural moisture, %	18.5	13.5
Water resistance, %	97.8	99.0

temperature range of $160 - 200$ and $650 - 700°C$, although with zeolite heated in the temperature range of $80 - 100$ and $160 - 200°C$, the reflections with interplanar distances of $d = 0.396$ and 0.297 nm become $1.05 - 1.2$ times more intense whereas their integral width increases $2 - 5$ times. The products of heat treatment of zeolite at temperatures of $80 - 100$, $160 - 200$, and $650 - 700°C$ are observed to be chemically more active than the initial rocks. For instance, their reaction with a saturated solution of $CaSO_4$ was 1.2, 1.98, and 1.7 times more intense, respectively.

An increase in the exposure duration at the final temperature from 1 to 4 h has an even greater thermal activation effect on zeolite and increases its reaction capacity. Dehydration proceeds within a wide temperature interval: first the least bonded water is removed and then the water with higher energy of bonds. The crystalline mineral lattice in this process does not undergo significant changes. However, exchange cations Na^+, K^+, and Ca^{2+}, to which water molecules are bonded in the zeolite structure, become gradually involved in the process; and the coordinates of a substantial part of exchange cations in zeolite mineral channels that are surrounded by diffuse shells consisting of water dipoles become modified.

The physiochemical characteristics of zeolite are important for working of deposits and for solving technological problems related to transportation, storage, and operation of zeolite materials for a particular technology. The physicomechanical properties of zeolite depend on the degree of zeolitization of rocks. The higher this degree, the lower the true and bulk density and the higher the porosity of the material layer. The mechanical strength of a rock is determined by the zeolite mineralization and the type of the cementing material. The water resistance of zeolite is related to the presence of argillaceous materials prone to swelling. The results of a comparative analysis of the properties of Sakhaptinskoe and Kholinskoe zeolite are given in Table 4, whose data indi-

cate that the Sakhaptinskoe zeolite has a higher degree of zeolitization.

The natural dispersion of zeolite is low and is caused by a high degree of aggregation of mineral grains. The granulometric fraction distribution diagrams (the dispersion analysis was performed using the sedimentation and the pipette method) slows that the main rock fractions of the Sakhaptinskoe deposit are grains with boundary sizes of $0.06 - 0.01$ and $0.01 - 0.005$ mm and that of the Kholinskoe deposit have a size of $0.06 - 0.01$ mm. The fine fraction yield is $25 - 27\%$, including $10 - 15\%$ of the fraction below 0.001 mm.

To identity the mineral composition of the main zeolite fractions, the chemical and x-ray phase analysis of the fraction samples taken in the course of dispersion analysis from natural zeolite and zeolite milled to a specific surface area of 3000 cm^2/g was carried out. The molar ratio of $SiO_2 : Al_2O_3$ in the fraction of $0.06 - 0.01$ and $0.01 - 0.005$ nm of natural zeolite and of zeolite milled to a specific surface area of 3000 cm^2/g amounted to, respectively, 9.36, 9.00 and 10.70, 10.00 (Sakhaptinskoe rock) and 10.24, 9.64 and 10.64, 9.83 (Kholinskoe rock). With decreasing particle size, the content of SiO_2 increases and the calcination loss grows, which corroborates the presence of amorphous silica. The maximum intensity of the diffraction reflections of clinoptilolite is registered on the diffraction patterns of the fraction with a grain size of $0.06 - 0.01$ mm, heulandite in the fraction of $0.01 - 0.005$ mm (Sakhaptinskoe rock) and $0.005 - 0.001$ mm (Kholinskoe rock). On the whole the quantitative distribution of zeolite mineral by fractions amounted to: $15 - 20\%$ for $0.25 - 0.06$ mm, $45 - 50\%$ for $0.06 - 0.01$ mm, $20 - 30\%$ for $0.01 - 0.005$ mm, and $5 - 10\%$ for $0.005 - 0.001$ mm.

Milling of rock to a specific surface area of 3000 cm^2/g regularly increases the yield of the fractions sized below 0.06 mm. Mineral aggregates of zeolite rock rather rapidly disintegrate under mechanical impact. The milling processes are even more efficient in the presence of water. Thus, with the component ratio of zeolite : water equal to 1 : 1 (mass), the residue on a No. 008 sieve after 4 h of wet grinding of Sakhaptinskoe rock was 0.02%. As the specific surface area grows from 3000 to 5000 cm^2/g, the intensity of the diffraction reflections of clinoptilolite ($d = 0.892$, 0.396, and 0.297 nm) increases by 8, 34, and 30% for Kholinskoe zeolite rock and by 90, 20, and 67% for Sakhaptinskoe rock; on further milling to a specific surface area of 7000 cm^2/g, the intensity virtually does not grow. The results of processing the diffraction patterns of the products of milling of zeolite rock suggest that the dispersion level characterized by the specific surface area of 5000 cm^2/g provides for optimum disintegration of clinoptilolite crystals, which contributes to the activation of the physicochemical and technological properties of mixed zeolite-bearing binders.

A similar dependence is observed in determining the hydraulic activity of zeolites with different degrees of milling. Thus, the activity of zeolite with a specific surface area of 3000 cm^2/g reacting with a saturated solution of $CaSO_4$

TABLE 5

Zeolite rock (3000 cm^2/g)	Quantity of soluble oxides, %, passing into extract		
	alkaline[*]		acid (Al_2O_3)[**]
	SiO_2	Al_2O_3	
Sakhaptinskoe	18.60	13.50	3.64
Kholinskoe	16.50	10.70	4.15

[*] 1 N alkali solution, reaction mixture temperature 80°C, reaction duration 24 h.

[**] 6 M hydrochloric acid solution, boiling for 3 h.

TABLE 6

Zeolite rock	Pozzuolanic activity, %			
	natural dispersion	specific surface area, cm^2/g		
		3000	5000	7000
Sakhaptinskoe	19.1	76.4	84.5	85.2
Kholinskoe	16.2	70.5	78.2	82.8

(method of M. I. Strelkov) varies from 350 to 370, that of zeolite with a specific surface area of 5000 cm^2/g varies from 380 to 390, and with 7000 cm^2/g it varies from 300 to 320. Hence an important technological inference is made, that zeolite rocks to be used in mixed zeolite-bearing binders should not be milled to more than 5000 cm^2/g.

At present it is impossible to evaluate the suitability of zeolite material for the production of binders without extensive studies of the physicochemical criteria that determine the possibilities of developing binders of increased water resistance. These physicochemical criteria represent the crystal-chemical factor, the hydraulic and pozzuolanic activities of zeolite, and its reaction capacity with respect to the initial components of the binder or to the products of their hydration. Such integrated studies have been performed on naturally disperse zeolite rocks and on the products of their milling with specific surface areas of 3000, 5000, and 7000 cm^2/g, as well as individual fractions of zeolite rocks (0.25 – 0.06, 0.06 – 0.01, 0.01 – 0.005, and less than 0.005 mm) sampled in the course of dispersion analysis and dried to a constant mass.

The crystal-chemical properties of zeolite characterize the specifics of the crystal structure of zeolite minerals consisting in the capacity of the "active" part of the aluminum silicate skeleton under the effect of various reactants to enter into reactions and form new compounds and allow for controlling these processes. The contents of active silica and alumina dissolved in the liquid phase of the zeolite – reactant system (Table 5), i.e., the quantities of SiO_2 and Al_2O_3 passing into the alkali extract and the amount of alumina dissolved in hydrochloric acid, were found by direct chemical analysis of the extracts, whereas changes in the crystal lattice of the main zeolite mineral, i.e., clinoptilolite, were registered by x-ray phase analysis.

The x-ray patterns of zeolites after reaction with 1 N alkali solution in thermostable conditions (temperature of 80°C for 24 h) registered a decreased by half intensity of the diffraction reflections of clinoptilolite ($d = 0.396$ and 0.297 nm) and the reflection with $d = 0.892$ nm decreased 20 times with a simultaneous 1.5 – 2 time-increase in the half-width of these diffraction maxima. According to x-ray analysis, treatment of zeolite in 1 N alkali solution leads to a structural modification of the crystal lattice of clinoptilolite

due to the dissolution of a part of the aluminum silicate skeleton of zeolite minerals. The diffraction patterns of zeolite treated with concentrated hydrochloric acid and its solutions (1 N and 6 M) in boiling indicate that clinoptilolite becomes depleted of aluminum to a different extent not causing destruction of its crystal lattice. The general decrease in the intensity of the background bands on the diffraction patterns correlates with the dissolution of the amorphous component of the zeolite rock. The obtained results (according to GOST 8269–76) make it possible to attribute the clinoptilolite-bearing rock considered to rocks with a high potential reaction capacity.

The pozzuolanic activity of rocks is understood as the capacity of the pozzuolana (usually amorphous) component of the rock in its natural state of dispersion to enter into a chemical reaction with calcium hydroxide within a short time at normal temperature and atmospheric pressure. This restriction makes it possible to exclude the effect of rocks that are chemically inert under normal conditions, such as, for instance, quartz which, being finely milled at an elevated temperature and pressure, reacts with calcium hydroxide and forms water-resistant compounds. It is precisely the presence of pozzuolana in zeolite rocks that contributes to the more intense binding of lime from the saturated solution and, which is especially important for air-cured binders, participates in the formation of water-resistant compounds within the short curing period. F. Massazza [11] proposed to determine the pozzuolanic activity of rocks by boiling the material in a saturated solution of calcium hydroxide for 1 h. The pozzuolanic activity of zeolite rocks in binding calcium hydroxide from a saturated solution is shown in Table 6.

The notion of hydraulic activity has usually a wider meaning, i.e., the capacity of finely milled (to dispersion less than 60 μm) rock to enter into chemical reactions with calcium hydroxide in static conditions of a saturated solution within 30 days. There is a known set of methods enabling one to evaluate the hydraulic activity of rocks with respect to lime and gypsum, including M. I. Strelkov's method based on studying the capacity of finely milled materials containing active alumina to chemically bind gypsum from the saturated solution in boiling. These methods were used to study the reaction capacity of zeolite rocks with respect to saturated solutions of calcium and magnesium hydroxides and salts: $Ca(OH)_2$, $Mg(OH)_2$, $MgCl_2$, $CaCl_2$, $MgSO_4$, $CaSO_4$ (Figs. 1 and 2).

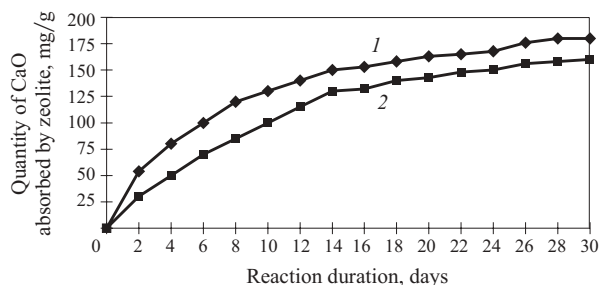X-ray analysis of the products of reaction of zeolite rocks with saturated calcium and magnesium solutions established

Fig. 1. Kinetics of binding Sakhaptinskoe (*1*) and Kholinskoe (*2*) zeolite rocks with calcium oxide from saturated calcium hydroxide solution.

Fig. 2. Reaction capacity of Sakhaptinskoe (*1*) and Kholinskoe (*2*) zeolite rocks reacting with saturated solutions of calcium and magnesium hydroxides and salts.

the virtually complete disappearance of background reflections related to the amorphous component of the rocks and the emergence of narrower reflections of zeolite minerals with a slightly decreased general background of the diffraction reflections.

The emergence of new crystalline phases is not registered, although an increase in the intensity of endothermic effects on the DTA curves is registered in the range of low ($70 – 200°C$), medium ($300 – 500°C$), and high ($700 – 800°C$) temperatures, which corroborates the formation of calcium hydrosilicates, hydroaluminates, and hydrosulfoaluminates in the x-ray-amorphous state presumably in an amount not more than $5 – 7\%$.

Consequently, the integrated study of zeolite rocks from the Sakhaptinskoe and Kholinskoe deposits demonstrated that the activity of clinoptilolite-heulandite rock is determined by many interrelated factors: the genetic type, the degree and form of zeolite mineralization, the crystal structure, and the physicochemical properties of zeolite minerals making up the rock, as well as the quantitative and qualitative compositions of exchange cations, the conditions of preparation of zeolite materials, and the "reaction" of the rock to them. Sakhaptinskoe zeolite rock manifested higher activity in testing. Of special importance is the existence of the amorphous component in zeolite rocks. This component enters into active chemical reactions with the binder component and in a short time forms water-resistant compounds. However, wide application of zeolite materials for binder production is delayed by technological problems. In order to use the potentially high activity of natural zeolite, the effects of mechanical and thermal activation or chemical reactants have to be used.

Based on the integrated studies of zeolite rocks from the Sakhaptinskoe and Kholinskoe deposits, individual approaches to using zeolites in mixed zeolite-containing binders (gypsum-zeolite, zeolite-magnesium, and lime-zeolite) were predicted.

In studying gypsum-zeolite binding systems, the capacity of clinoptilolite rocks to be being modified by calcium sulfate in joint low-temperature melting was established. 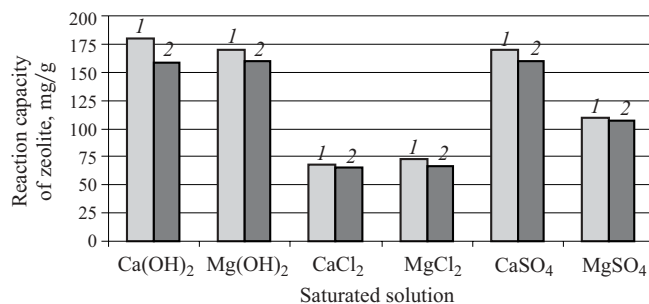Under the simultaneous effect of temperature and the pore liquid (a saturated solution of calcium sulfate), the pore space is saturated by the calcium sulfate solution, which leads to active participation of the zeolite rock in the process of curing and facilitates the formation of dense fine-pore and more water-resistant structures in the curing products.

Research on the specifics of the hydration and structure-formation process in zeolite-magnesium binders has revealed the effect of zeolite, which consists in the ability of clinoptilolite to modify the type of liquid medium (increasing pH), which accelerates the synthesis of magnesium hydroxide in the hydrolysis of salt according to the scheme $MgCl_2 \rightarrow MgOHCl \rightarrow Mg(OH)_2$ and, therefore, to deliberately influence the phase formation in the system. Furthermore, zeolite rock with its extended surface isolates non-water-resistant products of magnesium binder curing in the cavities and pores of the aluminosilicate matrix.

The persistently high hydraulic activity of zeolite rocks with respect to saturated solutions of calcium hydroxide motivates the study of lime-zeolite binders and silicate mixtures. It is observed in [3, 12] that in scalding of silicate systems based on lime-zeolite binders, Al-substituted tobermorite is formed, which decrease the cold resistance of the products. The favorable conditions for its synthesis imply long-term heat-moisture treatment, an increased temperature, and an alkaline medium in the reaction zone. The results of studying lime-zeolite binders indicated that the dependence of their main properties on the zeolite content is extremal Taking into account the specifics of the material composition of zeolite (the main part of silica exists in the bound state and the active silica content is around 20% including free quartz) and the behavior of zeolite under heat-moisture treatment (steaming and scalding), compositions for lime-zeolite binders were selected with a ratio of lime : zeolite : siliceous additives equal to $2 : 2 : 1$, which, converted to $CaO : SiO_2$ is equal to $0.9 – 1.0$.

Silicate mixtures were prepared using lime-zeolite binders and articles were molded. Scalding of the silicate articles was carried out in industrial autoclaves under the conditions of $2 – 4$ (6) for 2.5 h at 175°C and pressure of 0.8 MPa. The properties of obtained silicate products met the requirements of GOST 379–79.

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